Thomas-Fermi charge mixing for obtaining self-consistency in density functional calculations

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We present a new method for charge mixing in self-consistent density functional calculations which uses the Thomas-Fermi-von Weizsäcker equation to solve implicitly for the charge density response function to the potential. This approach has significant improvements over existing methods, particularly for inhomogeneous systems with large unit cells which commonly suffer from poor convergence due to charge sloshing.

Ab initio electronic structure calculations have become an integral part of the study of material properties. Density Functional theory (DFT)[1,2] is the most widely used ab initio approach in large scale materials simulations. Accurate predictions of mechanical properties, such as hardness, and electronic properties, such as conductivity, have made it an indispensable tool. As a result of ever increasing processor speeds and parallelization, larger and larger systems can be simulated with DFT based ab initio methods. Studying these larger systems is crucial for our understanding of complex systems/materials (surfaces, interfaces, defects, amorphous, etc.). However, as the size of the systems has become larger, the old problem of charge sloshing has resurfaced as a major issue. This problem comes from the slow convergence of the self-consistent potential in the potential (or charge) mixing schemes commonly used in these calculations. Here, a new more efficient potential mixing scheme[3] is tested, which uses an explicit Thomas-Fermi-von Weizsäcker equation to solve for the electronic response function of the system. The time spent for the solution of the Thomas-Fermi-von Weizsäcker equation is minimal for large systems as it only involves a minimization on the charge density and not the wavefunctions.

There are generally two approaches to handling the self-consistency in a DFT calculation. The first approach is to consider the total energy $E[\{\psi_i\}]$ as a function of only the Kohn-Sham[2] wave functions $\{\psi_i\}$ or the potential[4]. As a result, minimization methods (e.g., the conjugate gradient method) are used to directly minimize the functional $E[\{\psi_i\}]$[5]. There are drawbacks to such an approach as it requires a lot of computer memory and many computationally efficient linear algebra techniques cannot be used. The second and most heavily used approach is to change the non-linear minimization of $E[\{\psi_i\}]$ to an eigenvalue problem, but with an additional self-consistent requirement. We first require $\{\psi_i\}$ to satisfy the Kohn-Sham (eigenvalue) equation

$$[-\frac{1}{2}\nabla^2 + V_{in}(r) + \hat{V}_{nl}(r)]\psi_i = \varepsilon_i\psi_i. \qquad (1)$$

$V_{in}(r)$ is a given input potential, and $\hat{V}_{nl}(r)$ is the non-local potential existing only in pseudopotential calculations. Now for $\{\psi_i\}$ in this self-consistent field (SCF) calculation to be the minimum of $E[\{\psi_i\}]$, the potential $V_{in}(r)$ must equal the output potential $V_{out}(r)$, which is calculated from the occupied charge density $\rho(r) = \sum_{i\in occ} |\psi_i|^2$,

$$V_{out}(r) = \sum_R v_{ion}(r-R) + \int \frac{\rho(r')}{|r-r'|}d^3r' + \mu_{xc}(\rho(r)). \qquad (2)$$

Here $v_{ion}(r)$ is the local part of the ionic pseudopotential and $\mu_{xc}(\rho(r))$ is the LDA exchange-correlation potential.

Matching $V_{in}(r)$ with $V_{out}(r)$ is often done iteratively by producing a new $V_{in}^{m+1}(r)$ for the m+1th iteration from the $\{V_{in}^l(r), V_{out}^l(r)\}$ pairs of the last m iterations. The generation of $V_{in}^{m+1}(r)$ from $\{V_{in}^l(r), V_{out}^l(r)\}$ is called potential (charge) mixing, because in general, a mixture of $V_{in}^l(r)$ and $V_{out}^l(r)$ is used to generate the new $V_{in}(r)$. An often used linear mixing scheme is

$$V_{in}^{m+1} = (1-A)V_{in}^m + AV_{out}^m. \qquad (3)$$

However, it is easy to see why simple mixing schemes might lead to instability. Suppose $V_{sc}(r)$ is the final self-consistent local potential and let us denote $\delta V = V - V_{sc}$. The resulting output Coulomb potential, which is the dominant term and the cause of the charge sloshing, is given in reciprocal space q by,

$$\delta V_{out}^{Coul}(q) \cong \sum_{q'} \frac{-4\pi}{q^2}\chi(q,q')\delta V_{in}(q') \equiv \mathbf{J}\delta V_{in}. \qquad (4)$$

$\chi(q,q')$ is the susceptibility of the system defined as $\chi\delta V_{in} = \delta\rho_{out}$, which typically has a magnitude of order one.

From equations (3,4) we have $\delta V_{in}^{m+1} = [(1-A) + A\mathbf{J}]\delta V_{in}^m$. Notice that for a big system (or any system with one long dimension L), the smallest non-zero q in (4) [the zero q does not contribute] is $(2\pi/L)$. As a result, the magnitude of the maximum eigenvalue of $\mathbf{J}$, e_J, in (4) is large. If A is a constant larger than $||2/e_J||$, then the magnitude of the maximum eigenvalue of [(I-A)+AJ]

is larger than one, and the iterative process is divergent. This is the origin of the charge sloshing problem. A small error in δV_{in} will be amplified in δV_{out}. As a result, very small values for A (e.g., 0.01) need to be used for some calculations, which leads to very slow convergence. This problem associated with simple mixing schemes is discussed extensively in Annett's work.[7]

A better way to solve this problem is to use a matrix **A** in place of a scalar. Any **A** that leads to the magnitude of the maximum eigenvalue of [(I-**A**)+**AJ**] to be smaller than one will have a convergent iteration. The best **A** is the one which leads to [(I-**A**)+**AJ**]=0, thus $\mathbf{A} = (I - \mathbf{J})^{-1}$. This approach was used in Ref.[8] in the early days of ab initio calculations. Notice that, $I - \mathbf{J}(q, q')$ is just the dielectric matrix $\varepsilon(q, q')$. Unfortunately, in modern large scale calculations, the full dielectric matrix of the system is difficult to calculate, or estimate. Thus, often an approximate ε is used. One popular approximation is Kerker mixing[9], which uses the Thomas-Fermi dielectric function for the homogeneous electron gas, and leads to a diagonal **A**(q,q') proportional to $q^2/(q^2 + q_0^2)$. For homogeneous systems this damps the charge sloshing and significantly speeds up the convergence.

In the above discussion, only V_{in}^m and V_{out}^m of the m'th iteration are used to construct V_{in}^{m+1}. In principle, $\{V_{in}^l(r), V_{out}^l(r)\}$ for all the previous m iterations can be used. In the work of Dederichs and Zeller[10], following a detailed analysis, the constant A for each self-consistent iteration is readjusted according to the V_{in}, V_{out} of the previous cycles. The Broyden[11] method updates **A,** the inverse of the Jacobian matrix (charge dielectric matrix) of the non-linear function F[V_{in}] = (V_{in}- V_{out}[V_{in}]), with the current (V_{in},V_{out}) pair. However, it suffers from poor convergence most noticeably when Eq.(1) is not solved to high accuracy for every SCF cycle. In the initial SCF cycles, it is not efficient to have a high accuracy for the eigenvectors since we are far from the true potential.

A more recent approach[6] is to take a linear combination $V_{in}^{new} = \sum_l C_l V_{in}^l$, and ask for a minimum of $||V_{out}^{new} - V_{in}^{new}|| = ||\sum_l C_l [V_{out}^l - V_{in}^l]||$, with the condition $\sum_l C_l = 1$. This leads to a Pulay scheme[12]. However, for the Pulay scheme, the "in" and "out" potential are not mixed. Thus, after the $\{C_l\}$ are obtained, V_{in}^{new} and $V_{out}^{new} = \sum_l C_l V_{out}^l$ will be mixed according to (3), e.g., using the Kerker mixing leading to a Pulay-Kerker mixing scheme. G. Kresse and J. Furthmüller[13] showed the equivalence of the Pulay scheme to the modified Broyden method of D.D. Johnson.[14] This Pulay-Kerker (PK) method works well for homogeneous systems partly because the dielectric function of such systems can be approximated by the Thomas-Fermi dielectric function of a homogeneous electron gas (which is the basis of the Kerker mixing). However, for inhomogeneous system the homogeneous electron gas is no longer a good approximation for the dielectric function . For example, in a surface calculation, the PK method may not converge, as will be shown later.

In our new approach[3] we use the Thomas-Fermi-von Weizsäcker (TFW) equation[15] to solve the dielectric response for the given system directly, instead of using the homogeneous electron gas model. For small q, this step replaces the Kerker mixing of V_{out}^{new} with V_{in}^{new}. We will refer to this new method as the Pulay-Thomas-Fermi (PTF) mixing scheme. The Thomas-Fermi model has been widely used to describe the dielectric response function, and results compare well with other methods such as the random phase approximation.[16] The TFW formula has also been used to study the dielectric function.[17] The advantage of the TFW formula is that the charge density is smooth and realistic near the atomic nucleus and in the classically forbidden regions. Since an explicit solution of the TFW equation for a given inhomogeneous system is expected to describe the dielectric function well, especially for small q components (which is the cause of the charge sloshing), the use of it for potential mixing should speed up the convergence. For large systems, the time spent on solving the TFW equation for each self-consistent cycle is a relatively small fraction of the total time. Although more advanced kinetic energy functionals do exist,[18] we found that the use of the TFW form is sufficient for our purpose.

The full dielectric function $\varepsilon(r, r')$ is not solved explicitly which would be too expensive. We solve for it implicitly by calculating a new V_{in} from the V_{out} pair resulting from the Pulay mixing. The question we ask is that, given a V_{in} and V_{out} (with the corresponding charge density ρ_{out}) pair, according to the TFW formula, what is the new V_{in}^{next} that satisfies self-consistency. First, to reproduce the relationship between V_{in} and ρ_{out}, we have to modify the TFW formula. We will denote $\rho_{out}^{1/2}(r)$ as $\varphi_{out}(r)$, then the wave function type equation for the modified TFW formula is:

$$[-\frac{1}{2}\nabla^2 + \alpha\rho_{out}^{2/3}(r) + V_{in}(r) + V_{nl}(r)]\varphi_{out}(r) + \Delta W(r) = \varepsilon_F \varphi_{out}(r) \quad (5)$$

where $\alpha = (3\pi^2)^{2/3}$, and the $\alpha\rho_{out}^{2/3}$ term is the TF kinetic energy. $V_{nl}(r)$ is a local potential representing the nonlocal part of the potential in a Kohn-Sham pseudopotential wave function calculation. This is done by a weighted (by the atomic wavefunctions and their occupations) average of the s,p,d,... angular momentum dependent nonlocal atomic pseudopotentials. ε_F is the Fermi energy in the Kohn-Sham calculation. $\Delta W(r)$ is a term introduced to modify the TFW formula, so that ρ_{out} is the solution with V_{in} of (5). There are other ways to introduce this term such as replacing the single term by a potential multiplying $\varphi_{out}(r)$; but after some tests, we found that (5) is more stable. After $\Delta W(r)$ is calculated, the total TFW energy functional, from which (5) is derived, is:

$$E_{TFW}[\rho] = \int \{-\frac{1}{2}\rho^{1/2}(r)\nabla^2\rho^{1/2}(r) + \frac{3}{5}\alpha\rho^{5/3}(r)$$

$$+ \rho(r)[\sum_R v_{ion}(r-R) + V_{nl}(r)] \qquad (6)$$
$$+ E_{HXC}[\rho] + 2\Delta W(r)\rho^{1/2}(r)\}d^3r$$

where $E_{HXC}[\rho(r)]$ is the conventional LDA Hartree and exchange-correlation energy functional for a given charge density $\rho(r)$. The minimum energy of $E_{TFW}[\rho]$ is then solved using a conjugate gradient algorithm. The final solution gives $\rho_{out}^{next}(r)$ and the corresponding potential V_{out}^{next} equal to V_{in}^{next}, within the TFW formalism, and thus satisfying self-consistency. This is the TFW mixed potential which will be used for the next iteration of the Kohn-Sham equations Eq(1). However, since the non-local potential $V_{nl}(r)$ is treated in a very approximate way along with inherent limitations in the TFW formula, the large q components in $V_{in}^{next}(q)$ may be inaccurate. Consequently, we use the conventional Kerker mixing for large q components in $V_{in}^{next}(q)$.

We will now present some data for simulations using the TFW formula for planewave pseudopotential calculations using the LDA. While we have presented most of the formalism for our approach in the context of a planewave pseudopotential calculation we believe our method may also be advantageous for other DFT based approaches such as the full-potential linearized-augmented planewave (FLAPW) method.

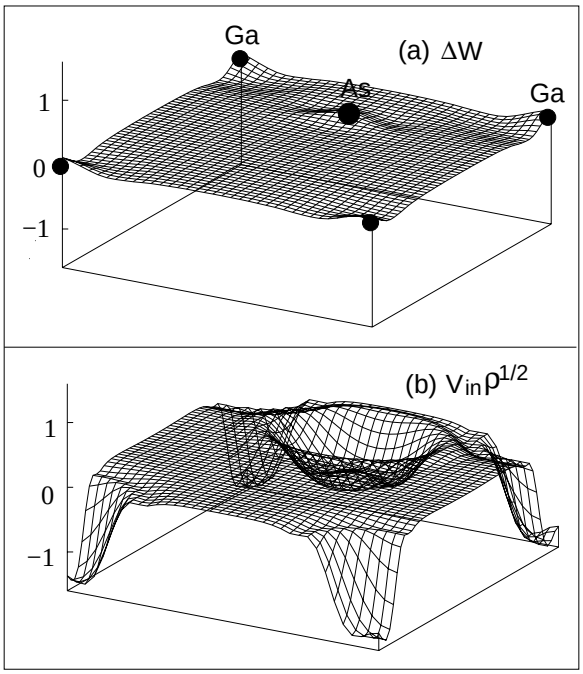

FIG. 1: (a) ΔW correction to the TFW equation in the (1-10) plane for bulk GaAs. (b) $V_{in}\rho^{\frac{1}{2}}$ in the (1-10) plane for bulk GaAs. ΔW and $V_{in}\rho^{\frac{1}{2}}$ are in the same arbitrary units.

In order to examine the role of the $\Delta W(r)$ correction to (5), Fig.1a shows the correction for bulk GaAs in the (110) plane. For comparison, Fig. 1b shows the plot of $V_{in}\rho^{\frac{1}{2}}$. We have used the final converged charge density and potential. Fig.1 shows $\Delta W(r)$ to be much smaller than $V_{in}\rho^{\frac{1}{2}}$ which illustrates the general accuracy of the TFW equation. However, $\Delta W(r)$ is appreciable near the atoms, where $V_{in}\rho^{\frac{1}{2}}$ is the largest, showing why it is necessary to introduce this term. The larger value of $\Delta W(r)$ near the nuclei can be attributed to the approximate treatment of the non-local pseudopotentials and to the kinetic energy which is highest near the nuclei.

In order to study the effects of inhomogeneity and system size on the performance of the different mixing methods, we chose to study one small surface system and three large systems of increasing inhomogeneity (small displacements from the ideal positions of the bulk, an interface and a surface). We simulated the semiconductor GaAs (with InAs for an interface) as it represents a relatively simple system that illustrates the advantages of our new method and also has technological importance. We only tested systems with no partial occupancies. All of the systems are extended in the (110) direction, each layer having 2 atoms. For the surface and interface calculations, we used the ideal bulk atomic positions. Since there are no surface states in the band gap[19] for the surface, similar findings would have resulted for the fully relaxed positions. Figs. 2(a)-(d) shows a comparison of convergence for the four systems with the new PTF mixing scheme, the Pulay-Kerker (PK) and Broyden (Br) schemes using an unconstrained conjugate gradient (CG) algorithm for the electronic minimization (diagonalization)[20]. We used 10 CG steps (updates) for each SCF cycle (which we found optimal for the systems studied), 25 Rydberg cutoff, and a 1x4x4 Monkhorst-Pack mesh for all calculations. The Y-axis is the difference in energy at each SCF cycle from the final converged total energy and the X-axis is the time per processor. All the simulations were carried out on a Cray T3E900. We chose time as our unit of measure since it is the fairest way to compare different methods where the amount of calculation and time for each SCF cycle is different. The convergence per SCF cycle can also be obtained from the graphs since each point on the graphs signifies one SCF step.

Fig. 2(a) shows the convergence for the small surface system containing 6 layers of GaAs in the (110) direction with 6 layers of vacuum (12 atoms total with 4 **k**-points in the irreducible Brillouin zone). The system is sufficiently small that Fig. 2(a) shows good convergence for all methods even though the system is highly inhomogeneous. At this system size, $\varepsilon(q,q')$ is a well-conditioned matrix and thus poses no problem for any of the different methods. Fig. 2(b) shows the convergence for a system of 40 layers of GaAs in the (110) direction with the atoms displaced randomly from their ideal positions, at most 0.028 Bohr (80 atoms total with 8 **k**-points). Fig. 2(b) shows little difference between the PTF and PK methods. With

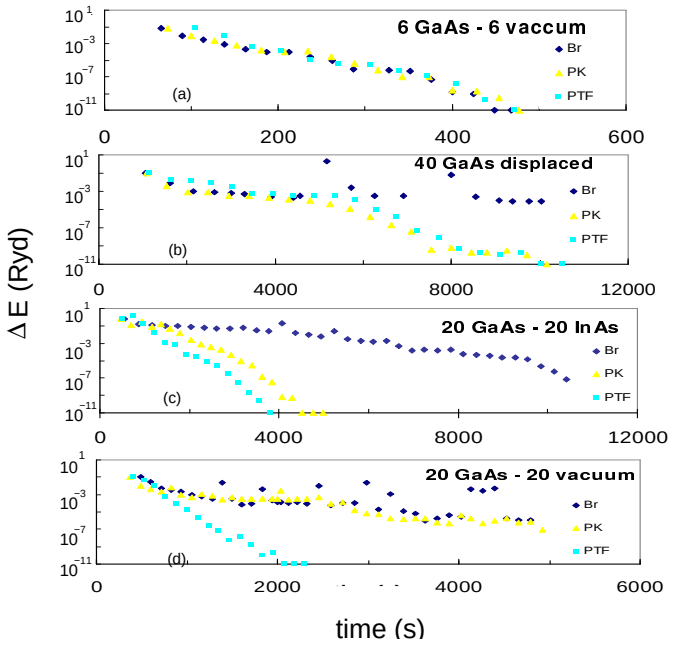

FIG. 2: (E - E_{final}) vs. time for (a) 6 layers GaAs – 6 layers vacuum, (b) 40 layers GaAs displaced randomly by small amounts, (c) 20 layers GaAs – 20 layers InAs, (d) 20 layers GaAs – 20 layers vacuum. Br, PK and PTF refers to the Broyden, Pulay-Kerker and Pulay-Thomas-Fermi charge mixing schemes. Each point represents one SCF step. All simulations were performed on a Cray T3E900 using 16 processors for (a) and 64 processors for (b),(c) and (d).

these small displacements from the ideal positions the Thomas-Fermi dielectric function for the homogeneous electron gas, which is used in the Kerker mixing, is still a close approximation to the true dielectric function. The Broyden method shows very poor convergence for this system. Fig. 2(c) shows the same data for an interface system of 20 layers of GaAs and 20 layers of InAs, both in the (110) direction (80 atoms total with 4 **k**-points). This system can be considered to be more inhomogeneous than 2(b) and we now start to see the advantages of the PTF scheme over the PK scheme. The PTF scheme converges about 15% faster. The dielectric function approximation used in the Kerker scheme is becoming less valid. The Broyden method again shows the worst performance. The time per SCF cycle in Fig. 2(b) compared to Fig 2(c) is roughly twice due to the decreased symmetry resulting in more **k**-points in the irreducible Brillouin zone. Fig. 2(d) shows the same information for a system of 20 layers of GaAs and 20 layers of vacuum (40 atoms total with 4 **k**-points) For this large, extremely inhomogeneous system we see significant differences between the PK and the PTF schemes with the PK scheme converging very slowly. The dielectric function approximation used in the Kerker scheme is highly inaccurate for large surface calculations. Comparing to the smaller surface calculation (Fig. 2(a)) and the other large, but less homogeneous systems (Figs. 2(b),(c)), Fig. 2(d) clearly shows the problems of convergence for the PK and Broyden schemes in dealing with large and inhomogeneous systems. The instability of the Broyden method can in part be attributed to over emphasis of new grdient information. The PTF method still converges rapidly for these types of systems.

In conclusion, we have presented the new Pulay-Thomas-Fermi method for potential (or charge) mixing for the self-consistent method of solving the Kohn-Sham equations. This method addresses the slow convergence and charge sloshing that occurs for large and inhomogeneous systems. The dielectric function $\varepsilon(q,q')$ at small q is calculated implicitly as V_{in}^{next} is obtained by solving the self-consistent Thomas-Fermi-von Weizsäcker equation with the charge density as the variable. A large surface calculation of GaAs shows the new method to be clearly superior to current methods. The benefit of the new method increases as inhomogeneity and system size increases.

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